

University of Groningen

Self-assembled-monolayer formation of long alkanedithiols in molecular junctions

Akkerman, Hylke B.; Kronemeijer, Auke J.; van Hal, Paul A.; de Leeuw, Dago M.; Blom, Paul W. M.; de Boer, Bert

Published in:
Small

DOI:
[10.1002/sml.200700623](https://doi.org/10.1002/sml.200700623)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2008

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Akkerman, H. B., Kronemeijer, A. J., van Hal, P. A., de Leeuw, D. M., Blom, P. W. M., & de Boer, B. (2008). Self-assembled-monolayer formation of long alkanedithiols in molecular junctions. *Small*, 4(1), 100-104. <https://doi.org/10.1002/sml.200700623>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

DOI: 10.1002/sml.200700623

Self-Assembled-Monolayer Formation of Long Alkanedithiols in Molecular Junctions**

Hylke B. Akkerman, Auke J. Kronemeijer, Paul A. van Hal, Dago M. de Leeuw, Paul W. M. Blom, and Bert de Boer*

The orientation of alkanedithiol molecules in self-assembled monolayers (SAMs) is of vital importance for their transport properties in molecular junctions. It is demonstrated that a too-low concentration of long alkanedithiols in ethanol leads to the formation of looped molecules, resulting in a 50-fold increase of the current through the SAM. X-ray photoelectron spectroscopy measurements show that high-concentration dithiol solutions result in a preferential standing-up phase. To obtain an almost full standing-up phase of 1,14-tetradecanedithiol (C14) a 30 mM concentration in ethanol is required, whereas a 0.3 mM concentration leads to a highly looped monolayer. The conduction through the full standing-up phase of C14 and C16 is in accordance with the exponential dependence on molecule length as obtained from shorter alkanedithiols.

Keywords:

- alkanedithiols
- molecular electronics
- molecular devices
- self-assembled monolayers

1. Introduction

In recent years, self-assembled monolayers (SAMs) have become an important subject in the field of molecular electronics.^[1,2] In device geometry, a wide variety of molecular junctions based on SAMs has been reported.^[3–6] Although large progress has been made in the understanding of the transport in molecular junctions,^[7] there is still disagreement in the obtained data from geometrically different molecular devices.^[8,9] Besides the important influence of contacts on

the absolute value of the conductance, the difference in molecular orientation and formation of the SAM on one of the electrodes is also a major factor that results in different conductance values for the same molecules. Self-assembled monolayers made from alkanethiolates have been investigated extensively.^[1,10,12] For alkane(mono)thiols it is now generally accepted from ellipsometry, Fourier transform infrared (FTIR) spectroscopy, near-edge X-ray absorption fine structure (NEXAFS) and X-ray photoelectron spectroscopy (XPS) measurements that the molecules arrange themselves locally in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure on Au(111) and are oriented at a $28\text{--}31^\circ$ angle with respect to the surface normal.^[1,10,12] Furthermore, with low-energy atom diffraction (LEAD) the outermost part of the molecules can be investigated and a second ordering of the SAM is found, corresponding to a $c(4 \times 2)$ superlattice^[1,10]. However, the adsorption of the sulfur atom to the Au(111) surface is still under debate. First of all, the fate of the hydrogen of the S–H group when the sulfur binds to the gold is still not unambiguously defined.^[1] Due to the chemisorption of the thiol to Au, the hydrogen is removed. Most likely driven by entropy gain, two hydrogen atoms result in the formation of H₂ or form water by oxidative conversion, the latter in solution. Secondly, the position of the sulfur atom on the Au(111)

[*] H. B. Akkerman, A. J. Kronemeijer, Prof. D. M. de Leeuw, Prof. P. W. M. Blom, Prof. B. de Boer
Molecular Electronics
Zernike Institute for Advanced Materials
University of Groningen
Nijenborgh 4, NL-9747AG Groningen (The Netherlands)
Fax: (+31) 503-638-751
E-mail: b.de.boer@rug.nl

Dr. P. A. van Hal, Prof. D. M. de Leeuw
Philips Research Laboratories, High Tech Campus 4
NL-5656AE, Eindhoven (The Netherlands)

[**] The authors gratefully acknowledge Jan Harkema, Edsger Smits, Hans Snijders, and Tom Geuns for their assistance. The research was financially supported by the Zernike Institute for Advanced Materials and NanoNed, a national nanotechnology program coordinated by the Dutch Ministry of Economic Affairs.

surface is still undetermined. Sulfur might bind to a three-fold hollow site, an on-top site,^[1] a different site for each molecule in the SAM,^[10] or it might be mediated by Au adatoms on the gold surface.^[13] On top of the uncertainties with regard to the Au–S bond the formation of SAMs based on the bifunctional α,ω -alkanedithiols is even less well understood, since both sides of the molecules can attach to gold. Self-assembled monolayers of 1,6-hexanedithiol by gas-phase deposition were found to be lying flat on the surface with both thiols attached.^[10,14] Assembled from solution, monolayers of several alkanedithiols form a standing-up phase attached to the surface through a single Au–S bond.^[15–17] Besides lying flat or standing up a third possibility also exists, where the chain “loops” back on itself and is anchored to the surface with both sulfur atoms. Kohale et al. showed with micromechanical cantilever measurements and Monte Carlo simulations that longer alkanedithiols (HS-(CH₂)_{*n*}-SH), with *n* > 10 can form a looping phase.^[18] The percentage of molecules in the looping phase increases with increasing chain length. The presence of a significant number of looped molecules is expected to strongly affect the electrical measurements on SAMs of alkanedithiols.

Recently, we have developed a technology to reliably fabricate large-area molecular junctions.^[9] In these junctions a highly conductive polymer blend (PEDOT:PSS) is used to fabricate the top contact on the SAM without forming electrical short circuits.^[9,19] For alkanedithiols in the range of C8 to C14, nonresonant tunneling was shown to be the electrical transport mechanism since the current density was found to be temperature independent and decrease exponentially with increasing molecule length (or tunneling-barrier width). The large-area junction also allowed for a direct determination of the dielectric constant from impedance measurements, which was found to be 2.1 for 1,14-tetradecanedithiol.^[19] Furthermore, assembling longer alkanedithiols in these molecular junctions gives us the unique possibility to simultaneously study their structural properties, and the relevance of their orientation on the electrical transport measurements, which depends on the conditions during the self-assembly.

2. Results and Discussion

The nomenclature used in this manuscript is as following: C8=1,8-octanedithiol; C10=1,10-decanedithiol; C12=1,12-dodecanedithiol; C14=1,14-tetradecanedithiol; C16=1,16-hexadecanedithiol. In Figure 1 the current density (*J*) versus the applied voltage (*V*) for alkanedithiol SAMs in the range of C8 to C16 is shown. All SAMs in Figure 1 are assembled from a 3 mM concentration in ethanol. The inset shows the exponential dependence of *J* at 0.1 V bias on molecule length. Two anomalous features can be observed. Firstly, and most striking is the absolute value of *J* for measurements on C16. The inset clearly shows that the current density obtained for C16 is not in agreement with the exponential decrease with length but is in fact higher than C14 at 0.1 V bias. Secondly, C14 shows a noticeable asymmetry

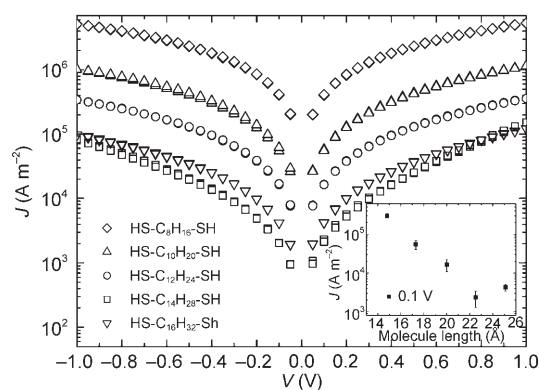


Figure 1. Current density versus applied voltage (*J*–*V*) for different alkanedithiols assembled from 3 mM ethanolic solution. The molecules range in length from C8 to C16. The inset shows the exponential dependence of *J* on the length of the molecule with the anomalous behavior of C16 (25.1 Å). Error bars represent standard deviation after averaging over at least 20 devices.

in the *J*–*V* characteristic, that is, $J(+1\text{ V})/J(-1\text{ V}) \approx 2$. Since it is reported that alkanedithiols form a partial looping phase with increasing molecule length,^[18] the observed features might be explained by this looping effect. Besides the molecule length, the ability to loop is also dependent on the concentration of the alkanedithiolate in ethanol during the self-assembly process. Looping of the molecules is likely to be sterically hindered when the concentration of the alkanedithiols in solution is increased. With increasing concentration the initial assembly process becomes more rapid^[10,12] and therefore the number of possible sites in the direct surroundings of the molecule for the second thiol (ω) to attach to the surface is drastically reduced.

The proposed mechanism is illustrated in Figure 2a–c based on a SAM of 1,14-tetradecanedithiol (C14). Figure 2a shows a perfectly ordered monolayer in the standing-up phase, most likely achieved at high concentrations of C14 in ethanol. In Figure 2b only a small percentage of looped molecules are present on the surface and are isolated in a matrix of molecules in the standing-up phase. The distance between the electrodes (*d*₁) remains the same as in the full standing-up phase, since the PEDOT:PSS molecules are too large to penetrate these small cavities created by the isolated looped molecules. The only difference resulting from the assembly from intermediate concentrations compared to the full standing-up phase is the contact between the SAM and the PEDOT:PSS. This contact is modified at the position of the looped molecules, where the conduction mechanism of through-bond tunneling might change to the less efficient through-space tunneling due to the presence of a gap between the looped molecules and PEDOT:PSS. When the concentration of the alkanedithiolate in ethanol is even further reduced, more molecules might loop back to the surface and the looping phase will be of more importance or might even become the dominant phase, as shown in Figure 2c. PEDOT:PSS can then penetrate from the surface of the standing-up phase to the looping molecules, reducing the effective thickness of the layer. The effective thickness is a combination of *d*₁ and *d*₂, with *d*₂ < *d*₁. Whether

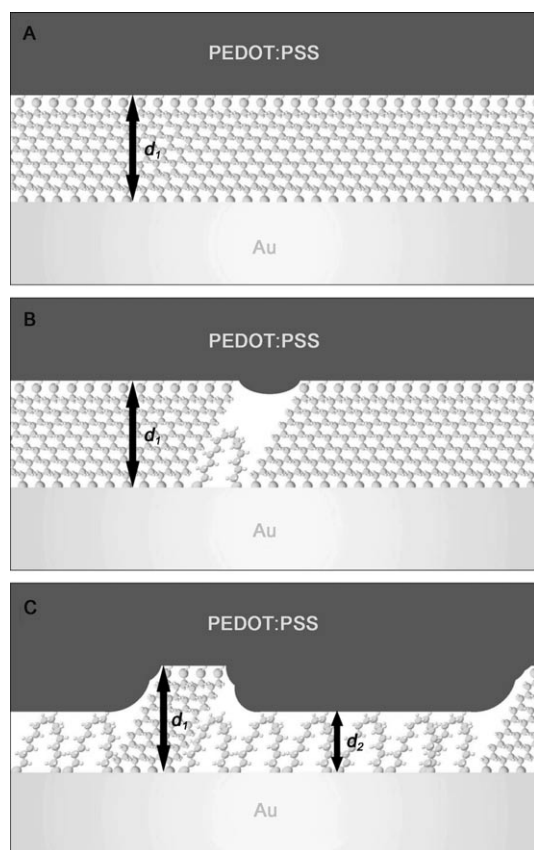


Figure 2. Illustration of self-assembled monolayers of C14 assembled from different concentrations. a) Assembly from high concentration leading to a full standing-up phase, b) a low percentage of isolated looping molecules resulting from an intermediate concentration, and c) a low concentration leading to a dominant looping phase.

through-bond or through-space is the electron-tunneling mechanism at locations of reduced thickness, this will increase the tunneling current noticeably compared to measurements on the full standing-up-phase monolayers assembled from high concentration. It should be noted that *high*, *intermediate* and *low* concentration are dependent on the length of the alkanedithiols used for the self-assembly. Since longer molecules are more susceptible for looping, the concentration for which this will have a noticeable effect will be higher compared to shorter alkanedithiols.

To determine the influence of the concentration of alkanedithiols in ethanol during the assembly process, large-area molecular junctions were fabricated from 0.3 mM, 3 mM and 30 mM concentration of C14 in ethanol, with an incubation time of at least 36 hours. As shown in Figure 1, the 3 mM concentration resulted in a slight asymmetric J - V characteristic and would correspond to the intermediate concentration, Figure 2b. Therefore, this asymmetry might be caused by the change and irregularity of the contact between the SAM and PEDOT:PSS, due to the relatively few looped molecules in the SAM. Plotted in Figure 3 are the J - V characteristics for C14, assembled from different concentrations.

Increasing the concentration during the assembly to 30 mM results in an almost complete standing-up phase. The J - V characteristic changes from slightly asymmetric to fully

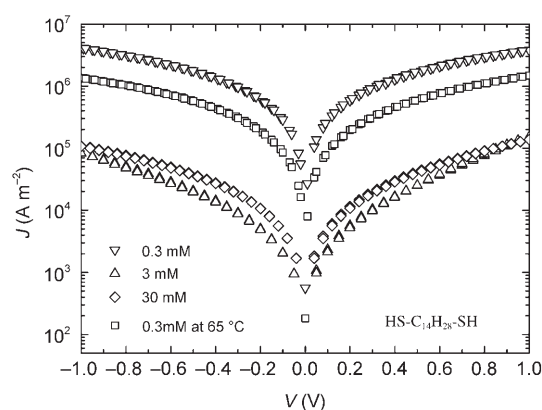


Figure 3. J - V characteristics of a large-area molecular junction based on C14 dithiol obtained at different concentrations and temperature during the self-assembly process. The almost complete looped phase of the SAM is present after assembly from a 0.3 mM concentration, which results in a 50-fold increase of the current compared to the densely packed and full standing-up phase assembled from a 30 mM concentration. The assembly of C14 at 65 °C results in a decrease of a factor of 3 at a 0.1 V bias, compared to the assembly at room temperature.

symmetric. Moreover, the absolute value of the current density at higher voltages is nearly equal compared to the devices from the 3 mM concentration. This confirms the suggested looping of a few molecules at 3 mM, where the distance between the contacts (or tunnel-barrier width) is equal to the full standing-up phase. The current density is increased by a factor of 50 at a bias of 0.1 V when the concentration during the assembly is reduced to 0.3 mM, a clear indication for a high percentage of looping molecules in the SAM and, consequently, a thinner layer for tunneling of charge carriers. The total increase in current is most likely also influenced by a change of contact resistance of the PEDOT:PSS to the SAM and a change in the number of tunneling pathways, in case of through-bond tunneling. To promote the detachment of the thiol to the gold and therefore increase the chances for a standing-up phase at low concentrations, C14 was assembled from a 0.3 mM concentration at an elevated temperature of 65 °C in a reflux setup. A decrease in the current with a factor of 3 at 0.1 V bias compared to the C14 from 0.3 mM concentration assembled at room temperature was observed. This would indeed correspond to a small increase of the number of molecules in the standing-up phase.

To verify the looping of the molecules at different concentrations, XPS studies of the assembled C14 monolayers were done on UV oxygen-cleaned gold films. The results are summarized in Table 1. It shows that for C14 monolayers the amount of unbound $^{35}\text{S-C}$ (S2p: 163.5 ± 0.1 eV) compared to the chemisorbed S-Au (S2p: 161.9 ± 0.1 eV) increases with increasing SAM concentration. These “raw” concentrations (at%) have to be corrected for the reduced peak intensity for the S-Au compared to the outer $^{35}\text{S-C}$ resulting in a more realistic picture.

A model analysis has been provided to convert the “raw” concentrations into more meaningful quantities.^[20] Assuming homogeneity in each layer, the thickness of the

Table 1. XPS results. "Raw concentrations" (at%) obtained directly from the peak areas measured at 45° showing the atomic concentrations (%) obtained on a monolayer of HS-C₁₄H₂₈-SH from low to high concentrations in ethanol onto a cleaned gold surface.

Molecules	Concentration [mM]	Au 4f	C 1s		O 1s	S-O _x	S 2p ¹ S-C	Au-S
			C _x H _y	C-O				
HS-C ₁₄ H ₂₈ -SH	0.03	59.9	36.0	0.3	0.7	-	0.4	2.8
HS-C ₁₄ H ₂₈ -SH	0.3	57.5	38.5	0.4	0.6	-	0.4	2.6
HS-C ₁₄ H ₂₈ -SH	3	33.6	54.7	3.5	3.0	0.6	3.1	1.7
HS-C ₁₄ H ₂₈ -SH	30	39.3	52.6	1.9	1.5	-	2.5	2.2

organic layers, the concentrations of the compounds in the layers and the coverage of the gold with sulphur (in atoms cm⁻²) can be calculated.^[21] Here, the monolayer is modeled using a four-layer model: Au/S-Au/C, O/¹S-C. The results for the layer thickness and the S-Au : ¹S-C ratio are shown in Figure 4. Clearly, the layer thickness of monolayers increases from 1 nm for low-concentrated solutions to about 2 nm for high-concentrated solutions. Together with this increase in layer thickness, the ¹S-C:S-Au ratio increases to 1 for higher-concentrated solutions as expected for a full standing-up phase. Using this model, a layer thickness of 1.9 nm is obtained for 30 mM HS-C₁₄H₂₈-SH. The length of C14 was calculated to be 22.6 Å, including a 2.3 Å Au-S bond.^[22] When a tilt angle of 30° is assumed, a layer thickness of 1.96 nm is expected, which is within the error margin of the layer thickness as obtained from the XPS measurement using the four-layer model. A high grafting density or coverage close to the maximum coverage of 4.67 × 10¹⁸ molecules m⁻² of alkane(di)thiols on Au(111) is obtained,^[20,23] indicating a "full" standing-up phase. For the

monolayers of C14 assembled from 0.03 and 0.3 mM concentration the peak intensity for the unbound ¹S-C was found to be very low compared to the bound S-Au. This implies that almost all C14 molecules are attached with both thiol end groups (α and ω) to the gold surface, that is, a large surface coverage with the looping phase. Besides HS-C₁₄H₂₈-SH, the concentration dependence for HS-C₁₂H₂₄-SH is also studied. A similar behavior is observed, as depicted in Figure 4. Increasing the concentration results in an increase in the layer thickness and in an improved ¹S-C:S-Au ratio becoming 1 for a sufficient concentrated solution. Hence, a preferential standing-up phase is observed for higher SAM concentrations. Interestingly, the full standing-up phase for HS-C₁₂H₂₄-SH as inferred from the layer thickness starts at a lower concentration compared to HS-C₁₄H₂₈-SH. This can be ascribed to the decreasing percentage of molecules in the looping phase with decreasing chain length.^[18]

Next, C16 was assembled at higher concentrations. From the inset in Figure 1 it is clear that a SAM of C16 assembled from a 3 mM concentration exhibits a large number of looped molecules and does not fit the exponential length dependency of the current density. Therefore C16 was assembled from a saturated solution (\approx 30 mM in ethanol). The exponential decrease of the current density with increasing molecule length is plotted in Figure 5, where C14 and C16 are assembled from a 30 mM concentration to form a standing-up phase SAM. Clearly, C16 assembled from a higher concentration does indeed lead to a significantly reduced current density (inset of Figure 5), due to a thicker

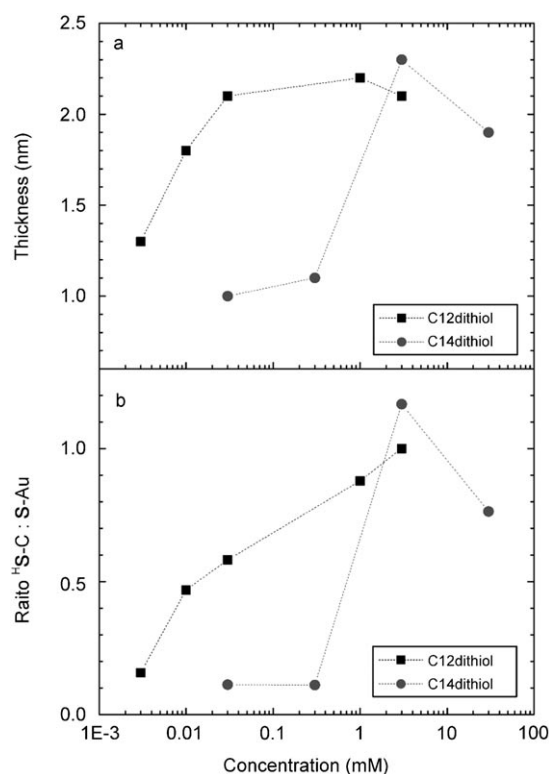


Figure 4. XPS results for concentration-dependent SAM formation of HS-C₁₄H₂₈-SH and HS-C₁₂H₂₄-SH. a) The layer thickness and b) the ¹S-C:S-Au ratio are based on a four-layer model calculation assuming homogeneity in each layer.

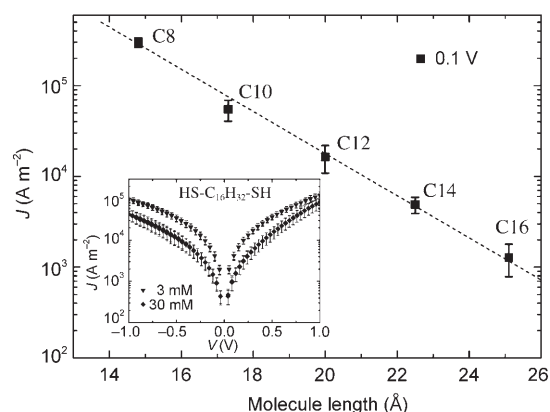


Figure 5. Current density J versus molecule length with C14 (22.6 Å) and C16 (25.1 Å) assembled from high concentration, that is, 30 mM, in ethanol. Compared to the assembly from a 3 mM solution C16 assembled at 30 mM has a majority of molecules in a standing-up phase and therefore C16 fits the exponential decrease of J with increasing molecule length. The inset shows the decrease of the current density for C16 when the concentration of C16 in ethanol is increased.

insulating layer for tunneling. A plot of the data in Figure 5 results in an excellent exponential decrease of the current density with increasing molecule length. Furthermore, it should be noted that a slight asymmetry was found for C16 at higher concentrations (30 mM) in the J - V characteristics, with $J(+1\text{ V})/J(-1\text{ V}) \approx 2$, the same asymmetry as that obtained with C14 at 3 mM. This confirms the expected length dependency for looping of alkanedithiol molecules when concentrations are kept constant: longer α,ω -alkanedithiols require higher concentrations of the molecules in solution to prevent looping from the ω -end thiol to Au.

3. Conclusion

We have fabricated large-area molecular junctions with C14- and C16-dithiol monolayers from different concentrations in ethanol and measured the influence of monolayer formation on the electrical output of the junctions. The percentage of longer alkanedithiol molecules that assemble in a standing-up phase and in a looping phase can be varied by systematically adjusting the concentration in ethanol. By decreasing the concentration of the alkanedithiolate in ethanol for the self-assembly process, a higher percentage of looped molecules is present in the monolayer, resulting in a large increase in current density and slightly asymmetric J - V characteristics. XPS data confirmed a preferential standing-up phase for monolayers of C14 and C12 assembled from highly concentrated solutions of alkanedithiolate in ethanol. Low-concentration solutions for longer alkanedithiols result in a monolayer with mainly looped molecules having both thiols attached to the gold. The electrical measurements on C14 and C16 reveal that only the conductance through the full standing-up phase is consistent with nonresonant tunneling as obtained from shorter alkanedithiols.

4. Experimental Section

The molecular junctions were processed similar to a previously described method.^[9,19] On a four-inch Si/SiO₂ wafer with a 500-nm thermally grown oxide layer an adhesion layer of 1 nm of Cr and 60 nm of Au are thermally evaporated. The typical RMS roughness of the Au bottom contact for 1 μm^2 is 0.5 nm. Subsequently, negative photoresist ma-N 1410 (Micro Resist Technology GmbH) was spin coated on the wafer and a prebake step on a 95°C hotplate eliminated the remaining solvents in the layer. Lithography was performed with a Karl Süss MA1006 maskaligner. Vertical interconnects are created in the photoresist layer by photolithography on top of the bottom Au electrodes, ranging from 10–100 μm in diameter. Annealing at 200°C in vacuum for 1 h ensured insolubility of the photoresist in ethanol. The complete wafer is then submersed for a minimum of 36 h in ethanol containing the self-assembling molecules. The synthesis of the molecules was done according to previously published procedure.^[9] After the self-assembly of the alka-

nedithiol molecules on the Au bottom electrode, the wafer was rinsed with ethanol, toluene, and isopropyl alcohol to remove any remaining alkanedithiol molecules. Subsequently, the water-based suspension of PEDOT:PSS (Baytron P HC V4, H.C. Starck GmbH & Co.) was spin coated and dried in a vacuum chamber. To decrease the surface tension of the PEDOT:PSS and improve the wetting on the SAM in the vertical interconnects, the surfactant FSO Zonyl 100 (Dupont) was added. Finally, a 150-nm Au top electrode was thermally evaporated on top of the PEDOT:PSS layer and the redundant PEDOT:PSS was removed by reactive-ion etching.

- [1] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103.
- [2] B. A. Mantooth, P. S. Weiss, *Proc. IEEE* **2003**, *91*, 1785.
- [3] J. He, B. Chen, A. K. Flatt, J. J. Stephenson, C. D. Doyle, J. M. Tour, *Nature Mater.* **2006**, *5*, 63.
- [4] J. G. Kushmerick, J. Naciri, J. C. Yang, R. Shashidhar, *Nano Lett.* **2003**, *3*, 897.
- [5] C. Zhou, M. R. Deshpande, M. A. Reed, L. Jones II, J. M. Tour, *Appl. Phys. Lett.* **1997**, *71*, 611.
- [6] N. B. Zhitenev, A. Erbe, Z. Bao, *Nanotechnology* **2003**, *14*, 254.
- [7] S. M. Lindsay, M. A. Ratner, *Adv. Mater.* **2007**, *19*, 23.
- [8] A. Salomon, D. Cahen, S. Lindsay, J. Tomfohr, V. B. Engelkes, C. D. Frisbie, *Adv. Mater.* **2003**, *15*, 1881.
- [9] H. B. Akkerman, P. W. M. Blom, D. M. de Leeuw, B. de Boer, *Nature* **2006**, *441*, 69.
- [10] F. Schreiber, *Prog. Surf. Sci.* **2000**, *65*, 151.
- [11] L. H. Dubois, R. G. Nuzzo, *Annu. Rev. Phys. Chem.* **1992**, *43*, 437.
- [12] A. Ulman, *Chem. Rev.* **1996**, *96*, 1533.
- [13] P. Maksymovych, D. C. Sorescu, J. T. Yates, Jr., *Phys. Rev. Lett.* **2006**, *97*, 146 103.
- [14] Y. B. Leung, M. C. Gerstenberg, D. J. Lavrich, G. Scoles, *Langmuir* **2000**, *16*, 549.
- [15] H. Rieley, G. K. Kendall, F. W. Zemicael, T. L. Smith, S. Yang, *Langmuir* **1998**, *14*, 5147.
- [16] M. Carot, M. J. Esplandiú, F. P. Cometto, V. A. Macagno, *J. Electroanal. Chem.* **2005**, *579*, 13.
- [17] V. B. Engelkes, J. M. Beebe, C. D. Frisbie, *J. Am. Chem. Soc.* **2004**, *126*, 14287.
- [18] S. Kohale, S. M. Molina, B. L. Weeks, R. Khare, L. J. Hope-Weeks, *Langmuir* **2007**, *23*, 1258.
- [19] H. B. Akkerman, R. C. G. Naber, B. Jongbloed, P. A. van Hal, P. W. M. Blom, D. M. de Leeuw, B. de Boer, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 11161.
- [20] C. van der Marel, M. Yildirim, H. R. Stapert, *J. Vac. Sci. Technol. A* **2005**, *23*, 1456.
- [21] For the full standing-up phase or complete-looping phase the layers on top of Au can be regarded as ordered homogeneous monolayers, and hence the model calculation adequately describes the quantification of the monolayer. However, minor problems with respect to exact quantification are expected for less homogeneous systems, which are possibly responsible for SAMs having both looped and standing-up phases. Therefore, a realistic estimation of the percentage of looped molecules in the monolayer formed is not trivial from XPS results.
- [22] Calculation of the molecule length was done with ACD/Labs 8.00 software.
- [23] C. M. A. Brett, S. Kresak, T. Hianik, A. M. O. Brett, *Electroanalysis* **2003**, *15*, 557.

Received: August 1, 2007

Published online on December 20, 2007